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TITLE: MANUFACTURE OF POSITIVE ELECTRODE
ACTIVE MATERIAL FOR ALKALINE BATTERY

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ABSTRACT:

PROBLEM TO BE SOLVED: To provide nickel oxyhydroxide, which is a positive electrode active material for an alkaline battery, having high purity and containing no impurities by treating nickel hydroxide, in which the content of cobalt is less than the specified value, and ozone and/or oxygen in an alkaline solution.

SOLUTION: A content of cobalt represented by $[(Co/(Ni+Co))]$ is less than 90 mol%. Nickel hydroxide powder having a particle size of 5-50 μm is dispersed in a sodium hydroxide aqueous solution having a

concentration of
approximately 4.5 M, while stirring, a mixed gas (mixed gas
of oxygen and
ozone) containing 10% ozone obtained with an ozone
generator by silent
discharge is passed into the suspension for a given time.
The powder obtained
is washed with hot water, then dried at 80°C to obtain
nickel oxyhydroxide.

The nickel oxyhydroxide is high purity β -nickel
oxyhydroxide in which a
phase in which alkali metal such as sodium is fixed to
between NiO layers
within crystal structure is not contained.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to an improvement of the manufacture conditions in the manufacture approach of the positive active material for alkaline cells.

[0002]

[Description of the Prior Art] Oxy-nickel hydroxide is used as positive active material of a Ni-Cd battery, a zinc nickel oxide battery, and a nickel hydrogen battery. Usually, in case these cells are manufactured, the active material of a discharge condition is used for a positive-electrode plate and a negative-electrode plate. That is, the plate which consists of cadmium hydroxide, a zinc oxide, a hydrogen storing metal alloy, or a hydrogen absorption metal is used for nickel hydroxide and a negative electrode at a positive electrode. It is also possible to be with the hydrogen storing metal alloy or hydrogen absorption metal which carried out oxy-nickel hydroxide to the active material of a charge condition, i.e., a positive electrode, and carried out occlusion of metal cadmium, metal zinc, or the hydrogen to the negative electrode, and to produce a cell to this, on the other hand.

[0003] The approach of compounding the compound whose valence [like nickel hydroxide, nickel nitrate, a nickel sulfate, or $K_2 [nickel (CN)_4]$] of nickel whose oxy-nickel hydroxide is it is divalent by oxidizing chemically using a powerful oxidizer like sodium-hypochlorite potassium peroxodisulfate in an alkaline water solution is reported by Z. Anorg. Chem., and 261, 26 and 1950. [JP, 6-31045, A, and] However, it is difficult for the class and presentation of the product obtained to change a lot, to stabilize it, and to obtain the oxy-nickel hydroxide of a high grade with reaction temperature or starting material, by this approach. Therefore, the sample of a high grade is hard to be obtained with the impurity contained in oxy-nickel hydroxide, and the nickel acid lithium which uses as a raw material the oxy-nickel hydroxide obtained by this approach has become the factor which is one to which the property as positive active material for lithium cells falls. In addition, whenever [electronic conduction / of nickel hydroxide] needs to make an electrode agent contain the conductive additive for raising whenever [electronic conduction / of electrode agents, such as graphite and metal powder,], although the attempt which compounds oxy-nickel hydroxide by oxidation electrochemical as a raw material also occurs nickel hydroxide in a multiple address notice, in order to advance a reaction, since it is very low, 10^{-12} - 10^{-14} S-cm⁻¹. Therefore, it is difficult to obtain pure oxy-nickel hydroxide.

[0004]

[Problem(s) to be Solved by the Invention] Although oxy-nickel hydroxide is used as positive active material of alkali rechargeable batteries, such as a Ni-Cd battery, a zinc nickel oxide battery, or a nickel hydrogen battery, as mentioned above, the reaction condition of a chemical synthesis method is very severe, and a problem is to be able to become the manufacture process which can supply a sample to stability. In order to solve this, reaction conditions, such as starting material, reaction temperature, and a synthesis procedure, need to be optimized.

[0005] However, the useful reaction condition is not established. Moreover, although a reaction will generate sulfate ion as an impurity if a peroxydisulfuric-acid salt is used for after synthetic reaction

termination (for example, an oxidizer), such an impurity is difficult to remove completely. Since this impurity becomes the big factor in which recognizing minute amount existence into oxy-nickel hydroxide also degrades the property as a cell active material, it is anxious for using the oxidizer which does not generate such an impurity.

[0006]

[Means for Solving the Problem] the manufacture approach of the positive active material for alkaline cells by this invention, and the content of cobalt -- 90-mol% -- $\{(Co/(nickel+Co))\}$ by having the process which processes the nickel hydroxide, ozone, or/and oxygen which are the following in an alkaline solution, it is characterized by obtaining the oxy-nickel hydroxide which does not contain an impurity and which is the positive active material for alkaline cells of a high grade.)

[0007]

[Embodiment of the Invention] this invention relates to the improvement of the manufacture approach of the positive active material for alkaline cells used for a Ni-Cd battery, a zinc nickel oxide battery, a nickel hydrogen battery, etc. of manufacture conditions -- the content of cobalt -- 90-mol% -- $\{(Co/(nickel+Co))\}$ it is characterized by having the process which processes the nickel hydroxide, ozone, or/and oxygen which are the following in an alkaline solution.)

[0008] Excluding an impurity, since the oxy-nickel hydroxide obtained by this approach is a high grade, it can obtain the alkaline cell excellent in discharge capacity and a charge-and-discharge cycle property.

[0009]

[Example] Hereafter, this invention is explained using a suitable example.

[0010] [Example 1] Aeration of the mixed gas (mixed gas of oxygen + ozone) containing 10% of ozone obtained by the ozonator (ozonizer) by silent discharge was carried out by the rate of flow of per minute 0.2 dm³ into liquid for 8 hours, agitating sodium-hydroxide water-solution 2L of 4.5M which distributed 100g of 5-50-micrometer nickel hydroxide powder. Then, hot water rinsing was carried out, it dried at the temperature of 80 degrees C for 2 hours, and oxy-nickel hydroxide A for alkaline cell positive active material by this invention was obtained.

[0011] potassium-hydroxide water-solution 2L of 4.5M held at [example 2] 60 degree C -- the content of cobalt with a particle diameter of 5-50 micrometers -- 15-mol% -- $\{(100g \text{ of nickel hydroxide powder which is } Co/(nickel+Co))\}$ is added.) Aeration of the mixed gas (oxygen + ozone mixed gas) containing 20% of ozone obtained by electrolyzing the sulfuric-acid solution of specific gravity 1.2 using a platinum electrode was carried out by the rate of flow of per minute 0.3 dm³ into liquid for 5 hours, agitating a solution. Then, hot water rinsing was carried out, and it dried at the temperature of 80 degrees C for 2 hours, and oxy-nickel hydroxide B for alkaline cell positive active material by this invention was obtained.

[0012] Powder X-ray diffraction pattern of the oxy-nickel hydroxide which was obtained in the [comparison examination] examples 1 and 2 and which is used as positive active material of the alkaline cell by this invention, and the nickel hydroxide which is the raw material (CuKAlpha) It is shown in Fig. 1. Output voltage set [200mA and a scanning speed] to 50kV, and the output current set the conditions of the X diffraction at this time to 4 degrees / min.

[0013] In addition, the nickel hydroxide powder whose (a) is a raw material, (b), and (c) are the oxy-nickel hydroxide prepared in examples 1 and 2, respectively.

[0014] The X diffraction pattern of the product C which it processed not with ozone but with peroxydisulfuric-acid sodium, and also was produced like the example 1 as a comparison was shown in (d).

[0015] Besides the oxy-nickel hydroxide which is the purpose product in (d), unreacted nickel hydroxide remains and this drawing shows that reaction yield is low. That oxidation reaction of the alkali water solution by the peroxydisulfuric-acid salt used as an oxidizer has checked the main reaction as side reaction can also guess that this is one of the causes.

[0016] Moreover, the quantum of the amount of the alkali-metal cation contained in the oxy-nickel hydroxide corresponding to (b), (c), and (d) was carried out with ion chromatography, respectively.

[0017] Consequently, in the oxy-nickel hydroxide (b) by this invention, and (c), although most alkali-

metal cations were not detected, in (d), existence of sodium ion was checked as an impurity. Since all of these oxy-nickel hydroxide are washing on the same conditions, it is thought that sodium ion is being fixed in the crystal structure.

[0018] It can be said that it is desirable to use the beta-oxy-nickel hydroxide of a high grade which does not contain such an impurity as a cell active material since it becomes the factor which checks the diffusion path of a lithium ion or a hydrogen ion, and causes the fall of an electrochemistry property when it uses as a raw material of a cell active material or a cell active material as for this impurity.

[0019] However, in the oxy-nickel hydroxide for alkaline cell positive active material (b) which becomes this invention, and (c), each is the beta-oxy-nickel hydroxide of a high grade, and the cell excellent in the electrochemistry property can be produced.

[0020] Production of a [cell evaluation trial] alkaline cell was performed as follows. the oxy-nickel hydroxide obtained in the examples 1 and 2 as positive active material -- as electric conduction material -- metal nickel -- as 5wt(s)% and a binder -- a carboxymethyl cellulose -- 5wt(s)% -- after having mixed, respectively, having added water, making it the shape of a paste and applying to the nickel network which is a charge collector, it dried at 100 degrees C and the positive-electrode plate whose magnitude is 25mmx25mm was manufactured.

[0021] 300ml of potassium-hydroxide water solutions of 5M was used for this one positive-electrode plate, two metal nickel plates of the same magnitude as a counter electrode, and the electrolytic solution, and the trial cell was manufactured. The reference electrode of mercury/mercury oxide was used for potential measurement of a positive electrode.

[0022] After charging these cells for 16 hours with the current density (rate of 10 time amount) of 25 degrees C and 3.0 mA/cm², it discharged to 0V with the same current density.

[0023] The discharge property of the oxy-nickel hydroxide A and B by this invention is shown in Fig. 2. The thing in the case of the positive-electrode plate C is also doubled and shown conventionally which was manufactured by the same approach using the oxy-nickel hydroxide which has the X diffraction pattern shown in Fig. 1 (d) as a conventional example for a comparison.

[0024] [Evaluation result] Fig. 2 shows that the positive-electrode plate equipped with about 290 mAh/g and the oxy-nickel hydroxide by this invention is excellent in an electrochemical property with the active material by about 250 mAh/g and this invention with the active material by the conventional method, when the discharge capacity of each positive-electrode plate is measured. Furthermore, when the charge-and-discharge cycle trial was performed on the same conditions and the capacity retention of the 300 cycle eye to initial capacity was compared, becoming 90% in B, becoming 60% in C, and excelling also in the cycle property by the cell using the oxy-nickel hydroxide by this invention was shown by A 80%.

[0025]

[Effect of the Invention] this invention relates to the improvement of the manufacture approach of the positive-active-material oxy-nickel hydroxide for alkaline cells used for a Ni-Cd battery, a zinc nickel oxide battery, a nickel hydrogen battery, etc. of manufacture conditions -- the content of cobalt -- 90-mol% -- $\{(Co/(nickel+Co))\}$ it is characterized by having the process which processes the nickel hydroxide, ozone, or/and oxygen which are the following in an alkaline solution.)

[0026] Excluding an impurity, since the oxy-nickel hydroxide obtained by the above-mentioned approach is a high grade, it can offer the alkaline cell excellent in discharge capacity and a charge-and-discharge cycle property.

[0027] Since the oxy-nickel hydroxide for alkaline cell positive active material by this invention is beta-oxy-nickel hydroxide of a high grade which does not contain the phase by which alkali metal, such as sodium, is being fixed between the layers of six layer of NiO(s) within the crystal structure, when this oxy-nickel hydroxide is used as an alkaline cell active material, since an impurity is hardly included, the capacity fall accompanying charge and discharge shows very few outstanding electrochemical properties.

[0028] So, industrial worth of this invention is size very much.

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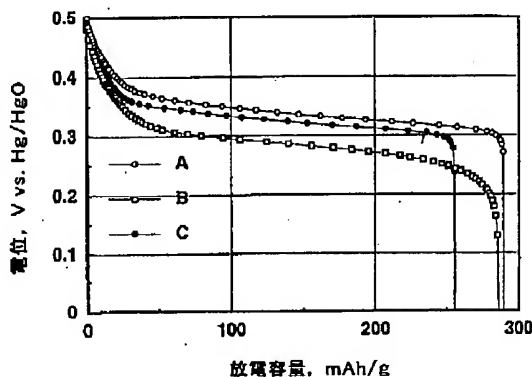
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(54) 【発明の名称】 アルカリ電池用正極活物質の製造方法

(57) 【要約】

【課題】 放電容量及び充放電サイクル特性に優れたアルカリ電池用正極活物質の製造方法を提供する。

【解決手段】 本発明になるアルカリ電池用正極活物質の製造方法は、コバルトの含有量が90mol% { (Co / (Ni + Co)) 未満である水酸化ニッケルとオゾン又は/及び酸素とをアルカリ性溶液中で処理する工程を備えたことを特徴とする。



【特許請求の範囲】

【請求項1】 コバルトの含有量が90mol% { (Co / (Ni + Co)) } 未満である水酸化ニッケルとオゾン又は/及び酸素とをアルカリ性溶液中で処理する工程を備えたアルカリ電池用正極活物質の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、アルカリ電池用正極活物質の製造方法における製造条件の改善に関する。

【0002】

【従来の技術】オキシ水酸化ニッケルは、ニッケルカドミウム蓄電池、ニッケル亜鉛蓄電池およびニッケル水素蓄電池の正極活物質として用いられている。通常、これらの電池を製作する際は、正極板、負極板ともに、放電状態の活物質が用いられる。すなわち、正極には水酸化ニッケル、負極には水酸化カドミウム、酸化亜鉛もしくは水素吸蔵合金または水素吸蔵金属からなる極板が用いられる。一方これに対して、充電状態の活物質、すなわち、正極にはオキシ水酸化ニッケル、負極には金属カドミウム、金属亜鉛もしくは水素を吸蔵した水素吸蔵合金または水素吸蔵金属をもちいて、電池を作製することも可能である。

【0003】オキシ水酸化ニッケルは、水酸化ニッケル、硝酸ニッケル、硫酸ニッケルまたは $K_2[Ni(CN)_4]$ のような、ニッケルの原子価が2価である化合物を、アルカリ性水溶液中で次亜塩素酸ナトリウム・ペルオキシ二硫酸カリウムのような強力な酸化剤を用いて、化学的に酸化することによって合成する方法が、特開平6-31045号や、Z. Anorg. Chem., 261, 26, 1950で報告されている。しかし、この方法では、反応温度や出発物質によって、得られる生成物の種類・組成が大きく変化し、安定して高純度のオキシ水酸化ニッケルを得ることが困難である。したがって、この方法によって得たオキシ水酸化ニッケルを原料とするニッケル酸リチウムは、オキシ水酸化ニッケル中に含まれる不純物によって高純度の試料が得られにくく、リチウム電池用正極活物質としての特性が低下する一つの要因となっている。なお、同報告において水酸化ニッケルを原料として電気化学的な酸化によってオキシ水酸化ニッケルを合成する試みもあるが、水酸化ニッケルの電子伝導度は $10^{-12} \sim 10^{-14} S \cdot cm^{-1}$ と非常に低いため、反応を進行させるためには、グラファイト・金属粉末などの、電極剤の電子伝導度を向上させるための導電性添加物を電極剤に含有させる必要がある。そのために、純粋なオキシ水酸化ニッケルを得ることは困難である。

【0004】

【発明が解決しようとする課題】オキシ水酸化ニッケルは、ニッケルカドミウム蓄電池、ニッケル亜鉛蓄電池またはニッケル水素蓄電池などのアルカリ二次電池の正極

活物質として用いられるが、前述したように、化学的な合成法の反応条件は非常にシビアで、安定に試料を供給できる製造プロセスとなり得るには問題がある。これを解決するには、出発物質・反応温度・合成手順などの反応条件の最適化が必要である。

【0005】しかしながら、有用な反応条件は確立されてはいない。また、合成反応終了後、たとえば酸化剤にペルオキシ二硫酸塩を用いると、反応によって不純物として硫酸イオンを生成するが、このような不純物は完全に除去することが困難である。この不純物はオキシ水酸化ニッケル中に微量存在するだけでも、電池活物質としての特性を劣化させる大きな要因となるので、このような不純物を生成しない酸化剤を用いることが切望されておる。

【0006】

【課題を解決するための手段】本発明によるアルカリ電池用正極活物質の製造方法は、コバルトの含有量が90mol% { (Co / (Ni + Co)) } 未満である水酸化ニッケルとオゾン又は/及び酸素とをアルカリ性溶液中で処理する工程を備えることによって、不純物を含まない、高純度のアルカリ電池用正極活物質であるオキシ水酸化ニッケルが得られることを特徴としている。

【0007】

【発明の実施の形態】本発明は、ニッケルカドミウム蓄電池、ニッケル亜鉛蓄電池およびニッケル水素蓄電池などに用いられる、アルカリ電池用正極活物質の製造方法の、製造条件の改善に関するものであり、コバルトの含有量が90mol% { (Co / (Ni + Co)) } 未満である水酸化ニッケルとオゾン又は/及び酸素とをアルカリ性溶液中で処理する工程を備えることを特徴としている。

【0008】この方法によって得られたオキシ水酸化ニッケルは、不純物を含まず、高純度であるため、放電容量および充放電サイクル特性にすぐれたアルカリ電池を得ることができる。

【0009】

【実施例】以下、本発明を好適な実施例を用いて説明する。

【0010】【実施例1】5~50 μm の水酸化ニッケル粉末100gを分散させた4.5Mの水酸化ナトリウム水溶液2Lを攪拌しながら、無声放電によるオゾン発生器(オゾナイザー)によって得られた10%のオゾンを含む混合ガス(酸素+オゾンの混合ガス)を、液中に毎分0.2 dm^3 の流速で8時間通気した。その後、湯洗し、80℃の温度で2時間乾燥して本発明によるアルカリ電池正極活物質用オキシ水酸化ニッケルAを得た。

【0011】【実施例2】60℃に保持した4.5Mの水酸化カリウム水溶液2Lに、粒子径5~50 μm のコバルトの含有量が15mol% { (Co / (Ni + Co)) } である水酸化ニッケル粉末100gを添加する。

溶液を攪拌しながら、比重1.2の硫酸溶液を白金電極を用いて電気分解することによって得られた20%のオゾンを含む混合ガス(酸素+オゾン混合ガス)を、液中に毎分0.3 dm³の流速で5時間通気した。その後、湯洗し、そして80℃の温度で2時間乾燥して本発明によるアルカリ電池正極活物質用オキシ水酸化ニッケルBを得た。

【0012】[比較検討] 実施例1および2において得られた、本発明によるアルカリ電池の正極活物質として用いるオキシ水酸化ニッケルと、その原料である水酸化ニッケルとの粉末X線回折図形(CuK α)を第1図に示す。このときのX線回折の条件は、出力電圧が50kV、出力電流が200mA、スキャンスピードが4°/minとした。

【0013】なお、(a)は原料である水酸化ニッケル粉末、(b)および(c)はそれぞれ実施例1および2において調製したオキシ水酸化ニッケルである。

【0014】比較として、オゾンではなく、ペルオキシ二硫酸ナトリウムで処理するほかは実施例1と同様に作製した生成物CのX線回折パターンを(d)に示した。

【0015】同図より(d)では、目的生成物であるオキシ水酸化ニッケルのほかに未反応の水酸化ニッケルが残存しており、反応率が低いことがわかる。これは、酸化剤として用いているペルオキシ二硫酸塩によるアルカリ水溶液の酸化反応が、副反応として主反応を阻害していることも原因の一つであると推察できる。

【0016】また、(b)、(c)および(d)に対応するオキシ水酸化ニッケルに含まれるアルカリ金属カチオンの量を、それぞれイオンクロマトグラフィーによって定量した。

【0017】その結果、本発明によるオキシ水酸化ニッケル(b)および(c)では、アルカリ金属カチオンはほとんど検出されなかったが、(d)の場合、不純物としてナトリウムイオンの存在が確認された。これらのオキシ水酸化ニッケルは、全て同じ条件で洗浄をおこなっているため、結晶構造内にナトリウムイオンが固定されているものと考えられる。

【0018】この不純物は、電池活物質または電池活物質の原料として用いたとき、リチウムイオンや水素イオンの拡散経路を阻害して電気化学特性の低下を引き起こす要因となるため、このような不純物を含まない、高純度の β -オキシ水酸化ニッケルを電池活物質として使用することが好ましいといえる。

【0019】ところが、本発明になるアルカリ電池正極活物質用オキシ水酸化ニッケル(b)および(c)では、いずれも高純度の β -オキシ水酸化ニッケルであり、電気化学特性に優れた電池を作製することができる。

【0020】[電池評価試験] アルカリ電池の作製は次

のようにした。正極活物質として、実施例1および2で得られたオキシ水酸化ニッケルに導電材として金属ニッケルを5wt%、結着剤としてカルボキシメチルセルロースを5wt%それぞれ混合し、水を添加してペースト状にして集電体であるニッケル網に塗布した後、100℃で乾燥し、大きさが25mm×25mmの正極板を製作した。

【0021】この正極板1枚と対極に同じ大きさの金属ニッケル板2枚と、電解液に5Mの水酸化カリウム水溶液300mlを用いて試験電池を製作した。正極の電位測定には、水銀/酸化水銀の基準電極を用いた。

【0022】これらの電池を25℃、3.0mA/cm²の電流密度(10時間率)で16時間充電した後、同じ電流密度で0Vまで放電をおこなった。

【0023】本発明によるオキシ水酸化ニッケルAおよびBの放電特性を第2図に示す。比較用の従来例として、第1図(d)で示されるX線回折パターンを有するオキシ水酸化ニッケルを用い、同様な方法で製作した従来正極板Cの場合のものも合わせて示す。

【0024】[評価結果] 第2図より、各正極板の放電容量を比較すると、従来法による活物質では約250mAh/g、本発明による活物質では約290mAh/gと、本発明によるオキシ水酸化ニッケルを備えた正極板は、電気化学的な特性に優れていることがわかる。さらに、同一条件で充放電サイクル試験を行い、初期容量に対する300サイクル目の容量保持率を比較したところ、Aでは80%、Bでは90%、Cでは60%となり、本発明によるオキシ水酸化ニッケルを用いた電池ではサイクル特性にも優れていることが示された。

【0025】

【発明の効果】本発明は、ニッケルカドミウム蓄電池、ニッケル亜鉛蓄電池およびニッケル水素蓄電池などに用いられる、アルカリ電池用正極活物質オキシ水酸化ニッケルの製造方法の、製造条件の改善に関するものであり、コバルトの含有量が90mol%{(Co/(Ni+Co))}未満である水酸化ニッケルとオゾン又は/及び酸素とをアルカリ性溶液中で処理する工程を備えたことを特徴とするものである。

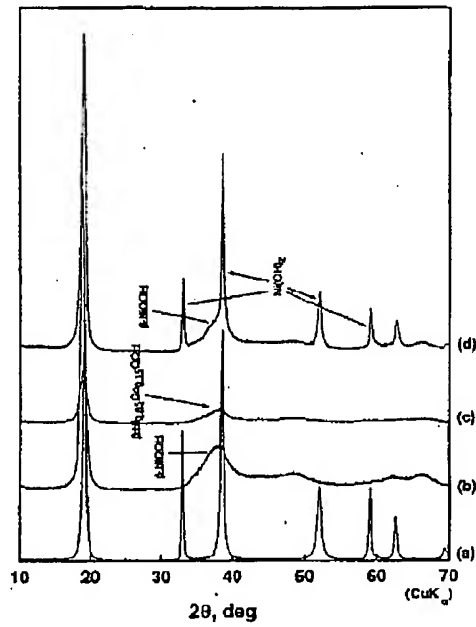
【0026】上記の方法によって得られたオキシ水酸化ニッケルは、不純物を含まず、高純度であるため、放電容量および充放電サイクル特性にすぐれたアルカリ電池を提供することができる。

【0027】本発明によるアルカリ電池正極活物質用オキシ水酸化ニッケルは、結晶構造内のNiO₂層の層間にナトリウムなどのアルカリ金属が固定されている相を含まない、高純度の β -オキシ水酸化ニッケルであるため、このオキシ水酸化ニッケルをアルカリ電池活物質として用いたとき、不純物をほとんど含まないために充放電にともなう容量低下が極めて少ない、すぐれた電気化学的特性を示す。

【0028】それゆえに本発明の工業的価値は極めて大である。

【図面の簡単な説明】

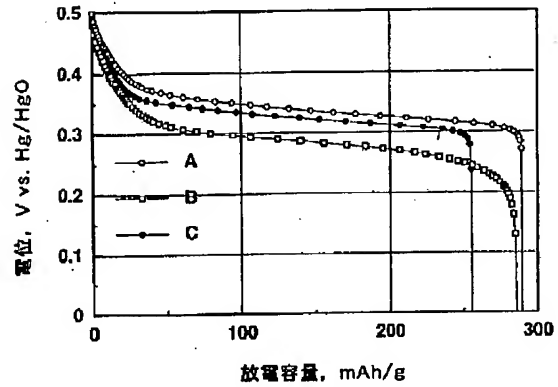
【図1】



【図1】 X線回折図形である。

【図2】 本発明による正極板A、Bおよび従来法による正極板Cの放電特性を示す図である。

【図2】



* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the initial chemical conversion approach of the initial chemical conversion approach of an active material, a battery, and a battery, the alkaline battery using the nickel electrode active material for alkaline batteries, and the active material concerned, and such an alkaline battery especially.

[0002]

[Description of the Prior Art] The nickel hydrogen battery which is a kind of an alkaline battery is being used as a source of power for portable electronic devices, such as a cellular phone, a small power tool, and a small personal computer. although the nickel hydrogen battery be excellent in the point that a nickel hydroxide system ingredient can be use for a positive electrode side , and it usually use a hydrogen storing metal alloy for a negative electrode side as an active material , respectively , and a high energy consistency can be attain , recently , in addition to it , amelioration of a high rate discharge property be make , and it have come to attract an attention also as a source of power of high power applications , such as a hybrid car which use both the electrical and electric equipment and a gasoline as an energy source , and an electric vehicle .

[0003] Since the above nickel hydrogen batteries have the large difference of the potential (oxygen evolution potential) which oxygen generates by disassembly of the electrolytic solution, and the potential (oxidation reaction potential) in which the oxidation reaction to the oxy-nickel hydroxide which is positive active material from nickel hydroxide occurs when used near ordinary temperature, generally they can expect high charging efficiency, but when a temperature rise is carried out by generation of heat at the time of charge and discharge etc., this potential difference becomes small and they are in the inclination for charging efficiency to fall. For this reason, although it is desirable to be used in the environment which raised heat dissipation nature and which cannot carry out a temperature rise easily as for a nickel hydrogen battery, since it is usually arranged in [, such as the inside of pocket electronic equipment, and an automatic in the car one,] the narrow space which cannot radiate heat easily and is used in many cases, it is difficult not to avoid a temperature rise but to maintain charging efficiency highly in many cases.

[0004] Then, about the nickel hydrogen battery, the amelioration for controlling decline in the charging efficiency under an elevated temperature is considered variously. for example, some nickel elements which constitute nickel hydroxide in a positive electrode in JP,3-78965,A -- the [of the periodic law] -- by permuting in II group element, cobalt, or these both, oxygen evolution potential is shifted to **, or oxidation reaction potential of nickel hydroxide is shifted to **, and even if it is under an elevated temperature, what was set up so that the difference of oxidation reaction potential and oxygen evolution potential might become large is indicated by this. Moreover, a lithium hydroxide is added to the potassium-hydroxide electrolytic solution which is the alkali electrolytic solution usually used in a nickel hydrogen battery, and the configuration in which oxygen evolution potential is shifted to ** by this is indicated by JP,7-45281,A. However, although the amelioration means of the charging efficiency

indicated by these official reports can improve the charging efficiency under an elevated temperature to some extent, the effectiveness is necessarily unsatisfying.

[0005] Then, what added the ytterbium or the ytterbium compound (for example, oxides, such as Yb_2O_3) to the nickel hydroxide of a positive electrode is indicated by JP,9-92279,A as an alkaline battery with which the elevated-temperature property has been improved remarkably. Moreover, what added the yttrium or the yttrium compound (Y_2O_3 and $\text{Y}(\text{OH})_3$ etc.) to the nickel hydroxide of a positive electrode similarly is indicated by JP,5-28992,A. Although the difference of the potential concerned and oxidation reaction potential tends to become large and can raise the charging efficiency under an elevated temperature in the positive electrode as a result of the oxygen evolution potential at the time of charge shifting to a ** side, these alkaline batteries Since it is usually hard to distribute an ytterbium, a ytterbium compound, an yttrium, or an yttrium compound in a nickel hydroxide, It is difficult from the first stage to acquire sufficient charging efficiency, and since these elements and compounds may bar formation of the conductive network in a positive electrode, they are difficult to maintain a high-rate-discharge property.

[0006] It is to realize the alkaline battery which can attain high charging efficiency, maintaining a high-rate-discharge property, even if the purpose of this invention is the case where cell temperature is an elevated temperature.

[0007]

[Means for Solving the Problem] The nickel electrode active material for alkaline batteries concerning this invention contains the 2nd component containing one sort of elements chosen from the element group which consists of the 1st component, a scandium and a lanthanum, the cerium, the praseodymium, the neodymium, the promethium, the samarium, the europium, the gadolinium, the terbium, the dysprosium, the holmium, ERUPIUMU, the thulium, the lutetium, the hafnium, the tantalum, the tungsten, the rhenium, the osmium, the iridium, the platinum, gold, and mercury of a nickel hydroxide system

[0008] Here, one mode of the 1st component is the mixture containing at least one sort in the nickel hydroxide with which different-species elements other than nickel hydroxide and a nickel element dissolved, and at least one sort in metal cobalt and a cobalt oxide.

[0009] Moreover, other modes of the 1st component are particle groups which consist of at least one sort in the group of the particle which covered for example, the nickel hydroxide particle with the cobalt compound, and the group of the particle which covered with the cobalt compound the nickel hydroxide particle to which different-species elements other than a nickel element dissolved. Here, a cobalt compound is at least one sort chosen from the group which consists of a compound of the high order cobalt exceeding for example, 1 cobalt oxide, divalent alpha mold cobalt hydroxide, divalent beta mold cobalt hydroxide, and divalent.

[0010] On the other hand, the 2nd component is the compound of the element chosen from the above-mentioned element group. In addition, in the 2nd component, the element chosen from the above-mentioned element group has the desirable metallic element chosen from the group which consists of a holmium, an erbium, a thulium, and a lutetium.

[0011] The 2nd component is in the above nickel electrode active materials for alkaline batteries of this invention by 0.5 - 20 weight ***** for example, to the 1st component 100 weight section.

[0012] The alkaline battery concerning this invention The 1st component of a nickel hydroxide system, and a scandium, A lanthanum, a cerium, a praseodymium, neodymium, a promethium, samarium, A europium, a gadolinium, a terbium, a dysprosium, a holmium, ERUPIUMU, a thulium, a lutetium, a hafnium, a tantalum, a tungsten, The positive electrode equipped with the active material containing the 2nd component containing one sort of elements chosen from the element group which consists of a rhenium, an osmium, iridium, platinum, gold, and mercury, It has the case where the separator arranged between the negative electrode and positive electrode which use a hydrogen storing metal alloy as an active material, and a negative electrode, a positive electrode, a negative electrode, and a separator are held, and the electrolytic solution arranged in a case at the list.

[0013] Here, a separator is a nonwoven fabric which is formed using the microfilament of for example, a

polyolefin resin system, and has a hydrophilic property.

[0014] As for the alkaline battery of this invention, cell temperature is usually set as 40-80 degrees C at the time of initial chemical conversion.

[0015] Moreover, the initial chemical conversion approach of the alkaline battery concerning this invention In the 1st component list of a nickel hydroxide system, a scandium, a lanthanum, a cerium, A praseodymium, neodymium, a promethium, samarium, a europium, A gadolinium, a terbium, a dysprosium, a holmium, ERUPIUMU, The positive electrode equipped with the active material containing the 2nd component containing one sort of elements chosen from the element group which consists of a thulium, a lutetium, a hafnium, a tantalum, a tungsten, a rhenium, an osmium, iridium, platinum, gold, and mercury, The process which sets the alkaline battery equipped with the case where the separator arranged between the negative electrode which uses a hydrogen storing metal alloy as an active material, and a positive electrode and a negative electrode, and a positive electrode, a negative electrode and a separator are held, and the electrolytic solution arranged in a case as the cell temperature of 40-80 degrees C, and is charged is included.

[0016]

[Embodiment of the Invention] The nickel electrode active material for alkaline batteries of this invention contains the 1st component of a nickel hydroxide system, and the 2nd component containing one sort of elements chosen from the fixed element group.

[0017] The 1st component used by this invention, i.e., the component of a nickel hydroxide system, is the group of the particle usually used for alkaline batteries, such as a nickel hydrogen battery, which uses nickel hydroxide as a principal component, and especially the class is not limited. Here, the nickel hydroxide with which different-species elements other than nickel (namely, except the configuration element of nickel hydroxide) dissolved in the crystal lattice of nickel hydroxide as nickel hydroxide which is a principal component for the purpose of raising more nickel hydroxide itself and the charging efficiency under an elevated temperature can be used (hereafter, these nickel hydroxide may be named generically and it may only be called "nickel hydroxide").

[0018] As a different-species element which dissolves to nickel hydroxide, zinc and cobalt can be mentioned, for example. Such a different-species element may be dissolving in the crystal lattice of nickel hydroxide as a simple substance (metal), and may be dissolving in the crystal lattice of nickel hydroxide as compounds, such as a hydroxide and an oxide. Moreover, as for the different-species element, two or more sorts of things may be dissolving to coincidence. Furthermore, the content of such a different-species element in the crystal lattice of nickel hydroxide is the weight conversion as a different-species element, and it is usually desirable to be set up at least to the weight of nickel hydroxide more than 2 weight sections.

[0019] Moreover, what mixed the accessory constituent of a cobalt system may be used to the principal component which consists of the above nickel hydroxide for the purpose of giving conductivity to nickel hydroxide and raising the utilization factor as a component of a nickel hydroxide system. As an accessory constituent of a cobalt system used here, the particle-like object (powdered material) of metal cobalt or cobalt oxide (for example, 1 cobalt oxide) can usually be illustrated. These may be suitably used together. Even if it is after the component of such a nickel hydroxide system, i.e., the 1st component, mixes the 2nd component mentioned later, the conductive network for raising conductivity is easy to be formed, and the charging efficiency and the high-rate-discharge property at the time of an elevated temperature become easy to attain a good active material.

[0020] Furthermore, the conductive network in an active material makes it to give conductivity to the front face of the particle of nickel hydroxide, and be easy to be formed as a component of a nickel hydroxide system in it, and in order to prevent that nickel hydroxide swells by the repeat of the charge-and-discharge cycle of a cell in coincidence, and a battery life is shortened, what covered with the cobalt compound the front face of the particle of the nickel hydroxide with which the particle or different-species element of nickel hydroxide dissolved may be used. Moreover, what mixed these suitably may be used. Although the cobalt compound used here is not limited especially if usually used in order to cover with the above-mentioned purpose the particle of the nickel hydroxide used as an active material,

it is at least one sort chosen from the group which consists of a compound of the high order cobalt preferably exceeding 1 cobalt oxide, divalent alpha mold cobalt hydroxide, divalent beta mold cobalt hydroxide, and divalent. Even if it is after the component of such a nickel hydroxide system, i.e., the 1st component, mixes the 2nd component mentioned later, the conductive network for raising conductivity is easy to be formed, and the charging efficiency and the high-rate-discharge property at the time of an elevated temperature become easy to attain a good alkaline battery.

[0021] An element with the 2nd fixed component used by this invention on the other hand, i.e., a scandium, (Sc) A lanthanum (La), a cerium (Ce), a praseodymium (Pr), neodymium (Nd), A promethium (Pm), samarium (Sm), a europium (Eu), A gadolinium (Gd), a terbium (Tb), a dysprosium (Dy), A holmium (Ho), ERUPIUMU (Er), a thulium (Tm), a lutetium (Lu), One sort of elements chosen from the element group of a hafnium (Hf), a tantalum (Ta), a tungsten (W), a rhenium (Re), an osmium (Os), iridium (Ir), platinum (Pt), gold (Au), and mercury (Hg) are included.

[0022] In the 2nd component used by this invention, especially the content gestalt of the element chosen from the above-mentioned element group is not limited. Namely, the element chosen from the above-mentioned element group should just be contained in the 2nd component with the gestalt of a simple substance or a compound. Here, as a compound of an element, an oxide, a hydroxide, a halogenide, and a carbonation object can be mentioned, for example. Moreover, two or more sorts of compounds of the element with the same compound of the element concerned may be mixed. In addition, a thing desirable as a compound of an element is one sort in an oxide and a hydroxide.

[0023] A thing desirable as the 2nd component used by this invention is the simple substance of a metallic element chosen from the group (it may be hereafter called a specific element group) which consists of Ho, Er, Tm, and Lu among above-mentioned element groups, and the group which consists of Er, Tm, and Lu more preferably, or the compound of the metallic element concerned. These elements and especially the nickel electrode equipped with the active material using the 2nd component containing those oxides have the large difference of oxygen evolution potential and the oxidation reaction potential of nickel hydroxide compared with other elements also in which [40 degrees C and 60 degrees C] temperature, as shown in drawing 1. This can control the oxidative degradation of the water which is for the active material of this invention containing such an element to shift oxygen evolution potential to a ** side more, and is the competitive reaction which this generates in the charge last stage of an alkaline battery, consequently can raise more effectively the charging efficiency of the alkaline battery at the time of an elevated temperature.

[0024] In the nickel electrode active material for alkaline batteries of this invention containing the 1st above component and the 2nd above component, as for the blending ratio of coal of the 1st component and the 2nd component, it is desirable to set the 2nd component as 0.5 - 20 weight section to the 1st component 100 weight section, and it is usually more desirable to set it as 2 - 5 weight section. When the blending ratio of coal of the 2nd component is under the 0.5 weight section, in an alkaline battery, there is a possibility that it may become difficult for the effectiveness of shifting oxygen evolution potential to ** to fall, and to raise the charging efficiency of the alkaline battery at the time of an elevated temperature. On the contrary, when the blending ratio of coal of the 2nd component exceeds 20 weight sections, there is a possibility that formation of a conductive network may be checked in the 1st component of an active material, consequently the high-rate-discharge property of an alkaline battery may fall. Moreover, since the 2nd component is not a component which participates in charge and discharge directly in an active material, it also has a possibility of the blending ratio of coal of the 1st component falling relatively as the blending ratio of coal increases, and the absolute magnitude of the 1st component decreasing as a result, and reducing the energy density of an alkaline battery.

[0025] The nickel electrode active material for alkaline batteries of this invention prepares separately the 1st above-mentioned component and the 2nd above-mentioned component, and if the 2nd component is added at a desirable above-mentioned predetermined rate and it mixes to homogeneity to the 1st component, it can prepare them. Thus, if it mixes with binders, such as a carboxymethyl cellulose, the prepared active material is usually prepared in the shape of a paste and this paste is applied to the porosity substrate made from nickel, it can constitute the positive electrode for alkaline batteries.

[0026] Since the nickel electrode active material for alkaline batteries concerning this invention adds the 2nd above component and is mixed to the 1st above-mentioned component, in the alkaline battery using it, oxygen evolution potential can be shifted to **, consequently the difference of the oxygen evolution potential concerned and the oxidation reaction potential by the side of the nickel hydroxide system component which is the 1st component can be set up greatly. Consequently, charging efficiency cannot fall easily at the time of an elevated temperature, and the alkaline battery using the nickel electrode active material of this invention can maintain high charging efficiency. In addition, in the active material of this invention, since the 2nd component is contained in the condition of having become independent of the 1st component, it cannot check formation of the conductive network in the 1st component easily. Therefore, the active material of this invention can raise the charging efficiency at the time of an elevated temperature in an alkaline battery, maintaining a high-rate-discharge property.

[0027] Next, with reference to drawing 2, the alkaline battery concerning one gestalt of operation of this invention is explained. In drawing, an alkaline battery 1 is a nickel hydrogen battery, and is mainly equipped with the positive electrode 3 arranged in a case 2 and the case 2 concerned, a negative electrode 4, a separator 5, and the electrolytic solution (not shown).

[0028] A case 2 is a in general cylindrical container which has opening 2a in the upper part, and the bottom surface part is set as the negative-electrode terminal. A positive electrode 3, a negative electrode 4, and a separator 5 are band-like members which all have flexibility, and a positive electrode 3 and a negative electrode 4 sandwiching a separator 5, after having been rolled round by the curled form, they are arranged in the case 2. moreover, the condition that, as for opening 2a of a case 2, the electrolytic solution was poured in into the case 2 -- it is -- an insulating gasket 6 -- inserting -- the obturation plate 7 -- liquid -- it is blocked densely. In addition, the obturation plate 7 has the positive-electrode terminal 8 on the top face. This positive-electrode terminal 8 is connected to the positive electrode 3 by the charge collector 9 which connects the obturation plate 7 and a positive electrode 3 electrically.

[0029] To porosity substrates made from nickel, such as a foaming nickel plate which has flexibility, the positive electrode 3 used in such an alkaline battery 1 applies the paste containing the above-mentioned nickel electrode active material concerning this invention to homogeneity, and is dried.

[0030] Moreover, to the pierced steel plank which has flexibility, a negative electrode 4 applies the paste containing the powder and thickener of a hydrogen storing metal alloy to homogeneity, and is dried. Although the hydrogen storing metal alloys used here are especially various kinds of things used in the nickel hydrogen battery and are not limited, they are AB2 system alloy which has the Laves phase structures of having CaCu5 mold structure, such as AB5 system alloy, MgCu2 mold, and MgZn2 mold, for example, AB system alloy which has CsCl mold structure, or A2B system alloy which has Mg2nickel mold structure.

[0031] A separator 5 consists of a nonwoven fabric of the permeability formed using polyolefin resin system fiber, such as for example, polyethylene resin fiber and polypropylene resin fiber, and the microfilament whose diameter of average fiber is about 3-25 micrometers preferably. As for this nonwoven fabric, it is desirable that the amount of eyes is set as 40 - 80 g/m2. When the amount of eyes is set up in this way, the nonwoven fabric concerned may be set as about [a 6-40 cc/cm2/second] permeability by the permeability of extent which can control an internal pressure rise of an alkaline battery 1, and the concrete target, controlling effectively that the hydrogen gas generated in the hydrogen storing metal alloy of a negative electrode 4 by the cell reaction moves to a positive-electrode 3 side. Consequently, in a positive electrode 3, the reduction reaction by hydrogen gas stops being able to happen easily, and the self-discharge of an alkaline battery 1 will be controlled.

[0032] Moreover, as for the nonwoven fabric which constitutes a separator 5, what has a hydrophilic property is desirable. The nonwoven fabric which has a hydrophilic property is realizable by the approach of irradiating ultraviolet rays to the nonwoven fabric concerned, and introducing a carboxyl group etc., after being immersed in the vinyl monomer solution containing the approach which is immersed in an oleum and carries out sulfonation processing of the nonwoven fabric which consists of above-mentioned fiber, and a photosensitizer in a nonwoven fabric. Moreover, also when the monomer of an acrylic-acid system uses beforehand that by which graft polymerization was carried out as

polyolefin resin system fiber, the nonwoven fabric which has a hydrophilic property can be obtained.

[0033] The separator 5 which has an above-mentioned hydrophilic property has ion-exchange ability preferably. In this case, the ion-exchange ability of a separator 5 has desirable 0.05 - 1 milliequivalent / g as an amount of exchange of potassium ion. When it has such ion-exchange ability, a separator 5 can adsorb various kinds of impurity ion, such as transition-metals ion eluted from NO₃⁻ which exists in the electrolytic solution, NO₂⁻, NH₄⁺, and a negative electrode 4, and can control effectively the self-discharge of the alkaline battery 1 resulting from these impurity ion.

[0034] The autolysis phenomenon of the oxy-nickel hydroxide (NiOOH) which incidentally generates the self-discharge of an alkaline battery 1 in the active material of a positive electrode 3 at the time of charge of an alkaline battery 1, And above-mentioned NO₃⁻ which is the impurity which may be contained in a positive electrode 3, In the shuttle effectiveness 3 by ion, such as NO₂⁻ and NH₄⁺, i.e., a positive electrode, NO₂-ion oxidizes to NO₃-ion, and it is regarded as what is produced according to the phenomenon in which NO₃-ion is returned to NO₂-ion in a negative electrode 4 at coincidence etc.

[0035] Furthermore, the electrolytic solution used in this alkaline battery 1 is various kinds of alkali water solutions, and although they are not limited especially, it is a water solution in which the potassium hydroxide, the lithium hydroxide, the sodium hydroxide, etc. were dissolved, for example.

[0036] Since the above-mentioned nickel electrode active material applied to this invention in a positive electrode 3 is used for the above-mentioned alkaline battery 1 concerning this invention, it can shift oxygen evolution potential to **, consequently can set up greatly the difference of the oxygen evolution potential concerned and the oxidation reaction potential by the side of the nickel hydroxide system component which is the 1st component. Consequently, this alkaline battery 1 can attain high charging efficiency, maintaining a high-rate-discharge property at the time of an elevated temperature.

[0037] In addition, as for the above-mentioned alkaline battery 1, it is usually desirable to set up and use the temperature at the time of initial chemical conversion for 40-80 degrees C. When the temperature at the time of initial chemical conversion is set up in this way, in a positive electrode 3, the dissolution or distribution into the 1st component of the 2nd component contained in a nickel electrode active material is easy to be promoted, and it is easier to shift oxygen evolution potential to **. Consequently, as for an alkaline battery 1, the difference of oxygen evolution potential and oxidation reaction potential becomes larger, and the charging efficiency at the time of an elevated temperature will be raised more.

[0038] In addition, when the temperature at the time of initial chemical conversion is set up more highly than 80 degrees C, there is a possibility that the electrolytic solution may begin to leak outside from a case 2, and the corrosion of a hydrogen storing metal alloy becomes easy to advance in a negative electrode 4, and the life of an alkaline battery 1 may become short as a result.

[0039] Incidentally, as the approach of initial chemical conversion, the temperature of an alkaline battery 1 is set as the above-mentioned range, and it is in the condition, after charging by the charging current of 1/20 or less CmA for 10 or less hours, the approach of charging by the charging current of 1/10 or more CmAs for further 10 hours or more is employable, but as long as a temperature setup is made above, other charge approaches may be adopted, for example.

[0040]

[Example] The element compound (B) which an example 1 - 14(manufacture of positive electrode) alpha mold cobalt hydroxide are covered by the front face, and zinc and cobalt indicate to be 3 weight sections and the powder (A) of nickel hydroxide by which 6 weight sections dissolution was carried out to Table 1, respectively was mixed by the weight ratio of A:B=96.5:3.5, and positive active material was obtained. Next, the obtained active material 80 weight section and the carboxymethyl-cellulose water-solution 20 weight section were mixed, and the paste was prepared. After applying this paste to the nickel porous body substrate which is a charge collector at homogeneity and drying, the porous body substrate was pressurized and cut in the electrode size for the cells of AA size. Thereby, capacity obtained the positive electrode of 1,500mAh(s).

[0041]

[Table 1]

表 1

実施例	元素化合物
1	Pr_6O_{11}
2	Nd_2O_3
3	Sm_2O_3
4	Eu_2O_3
5	Gd_2O_3
6	Tb_4O_7
7	Dy_2O_3
8	Ho_2O_3
9	Er_2O_3
10	Tm_2O_3
11	Lu_2O_3
12	HfO_2
13	Re_2O_7
14	IrO_2

[0042] (Manufacture of a negative electrode) The presentation of $\text{MmNi}_3.5\text{Co}_0.8\text{Mn}_0.4\text{aluminum}_0.3$ (Mm means the misch metal which is the mixture of rare earth elements, such as La, Ce, Pr, Nd, and Sm.) the following examples -- also setting -- being the same -- the thickener was added to the hydrogen storing metal alloy powder which has the CaCu5 mold structure shown, and the paste was prepared. After applying this paste to the pierced steel plank and drying, the pierced steel plank was pressurized and cut in the electrode size for the cells of AA size. This obtained the negative electrode.

[0043] (Manufacture of a nickel hydrogen battery) The acrylic acid involved in an above-mentioned positive electrode and an above-mentioned negative electrode on both sides of the separator which consists of a polypropylene resin system nonwoven fabric by which graft polymerization was carried out, and has arranged this in the case of a cylindrical shape. And concentration poured in the electrolytic solution with which the potassium-hydroxide water solution and concentration of 6.8 mol/dm³ consist of mixed liquor with the lithium-hydroxide water solution of 0.5 mols/dm³ into the case concerned, and capacity manufactured the alkaline battery (nickel hydrogen battery) of the cylindrical shape AA size sealing form of 1,500mAh(s).

[0044] Except for the point of having not used the element compound shown in example of comparison 1 table 1, the positive electrode was manufactured like the case of examples 1-14, and the same nickel hydrogen battery as the case of examples 1-14 was manufactured using this positive electrode. In addition, the capacity of the positive electrode manufactured here was 1,500mAh.

[0045] After pouring in the electrolytic solution and sealing each nickel hydrogen battery of evaluation 1 examples 1-14 and the example 1 of a comparison, it was left for 2 hours, and initial chemical conversion of the cell temperature was first maintained and carried out to 40 degrees C after that. Here, after charging cell temperature according to the charging current of 1/50CmA in the condition of having maintained at 40 degrees C for 10 hours, it charged by the charging current of 1/10CmA for 10 hours. And charge-and-discharge processing of 1 cycle eye was carried out after this initial chemical conversion by carrying out constant-current discharge of the cell concerned until cell voltage is set to 1.0V by the discharge current of 1/5CmA. Next, in the charge-and-discharge processing after a two-cycle eye, constant-current charge was carried out by the charging current of 1/10CmA for 15 hours, and constant-current discharge was carried out to 1.0V according to the discharge current of 1/5CmA.

[0046] The charging efficiency under a temperature environment (20 degrees C, 50 degrees C, 60 degrees C, and 70 degrees C) was investigated about each cell after above-mentioned charge-and-

discharge cycle processing in the place by which the discharge capacity of each cell was stabilized. Here, keeping cell temperature at 20 degrees C, 50 degrees C, 60 degrees C, or 70 degrees C, respectively, charge and discharge were repeated on the same conditions as an above-mentioned two-cycle one or subsequent ones until discharge capacity became fixed, and discharge capacity in that case was made into charging efficiency. A result is shown in drawing 3. In addition, drawing 3 shows the discharge capacity (charging efficiency) at the time of carrying out constant-current discharge by the discharge current of 0.2CmA(s) in the cell temperature of 20 degrees C as criteria (100%). Compared with the cell of the example 1 of a comparison, as for the cell of examples 1-14, drawing 3 shows that charging efficiency cannot fall easily, even when cell temperature is an elevated temperature. Especially the cell of examples 9, 10, and 11 is understood that charging efficiency is high under a 60-degree C temperature environment.

[0047] About the cell of evaluation 2 example 11 and the example 1 of a comparison, the temperature at the time of the initial chemical conversion in evaluation 1 was set as 20 degrees C, 40 degrees C, 60 degrees C, and 80 degrees C, respectively. And the charging efficiency at the time of setting cell temperature as 60 degrees C was investigated like the case of evaluation 1 about these cells. A result is shown in drawing 4. Drawing 4 shows that charging efficiency increases it further when the temperature at the time of initial chemical conversion is set as 40 degrees C or more, although it turns out that charging efficiency is increasing remarkably compared with the cell of the example 1 of a comparison in the cell of an example 11 even when the temperature at the time of initial chemical conversion is 20 degrees C.

[0048] Except for the point using what mixed what is shown in Table 2 as an element compound (B) at a rate shown in this table, the positive electrode was manufactured like the case of examples 1-14 to the (Powder A) 100 weight section of the nickel hydroxide used in 15 to example 17 examples 1-14. And the same nickel hydrogen battery as the case of examples 1-14 was manufactured using this positive electrode.

[0049] About each cell of evaluation 3 examples 15-17, initial chemical conversion was carried out at 40 degrees C by the same approach as the case of evaluation 1, and the charging efficiency under a 60-degree C temperature environment was investigated like the case of evaluation 1 after that. A result is shown in Table 2. From Table 2, in a positive electrode, the cell of each example is understood that charging efficiency is high compared with the case (the example 1 of a comparison: refer to drawing 4) where such an element compound (B) is not included, when the element compound (B) is being mixed in the range of 0.5 - 20 weight section to the (Powder A) 100 weight section of nickel hydroxide.

[0050]

[Table 2]

表 2

実施例	元素化合物	混合量 (重量部)	充電効率 (%)
15	Gd_2O_3	0.5	65
		3.5	70
		5	71
		10	68
		20	69
		25	70
16	Er_2O_3	0.5	86
		3.5	87
		5	88
		10	87
		15	86
		20	86
17	HfO_2	0.5	67
		3.5	70
		5	70
		10	71
		20	71
		25	70

[0051] Moreover, what carried out 25 weight sections mixing of the element compound (B) is further set up about the cell of the example 16 which carried out initial chemical conversion at 40 degrees C, and the result of having investigated the high-rate-discharge property under a 20-degree C temperature environment is shown in drawing 5. In addition, a high-rate-discharge property here carries out constant-current charge of the cell by the charging current of 1/10CmA for 15 hours, and is the result of investigating by carrying out constant-current discharge to 1.0V by the discharge current of CmA, 1CmA, and 3CmA(s) 1/2 after that. Drawing 5 shows that the high-rate-discharge property is falling, although charging efficiency is high when, as for the cell of an example 16, the mixed rate of an element compound (B) exceeds 20 weight sections (refer to Table 2). In a positive electrode, formation of a conductive network becomes inadequate, and this is considered for the energy density of a cell to fall, when many element compounds (B) are mixed from 20 weight sections in positive active material.

[0052] Cobalt hydroxide was covered to the nickel hydroxide particle which carried out solid-solution addition of example 18 (manufacture of a positive electrode) zinc, and the cobalt. 2035 % of the weight of Lu(s) as the 95 % of the weight of the 1st component which consists of this nickel hydroxide particle group, and the 2nd component was mixed, and positive active material was prepared.

[0053] Next, the obtained positive active material and 2% water solution of a carboxymethyl cellulose were mixed, and the paste was prepared. And after the surface density of 450g/m², and porosity applied

this paste to the nickel metal porosity substrate which is about 95% at homogeneity and dried, the porous substrate was pressurized and cut in the electrode size for the cells of AA size. This obtained the positive electrode.

[0054] (Manufacture of a negative electrode) The hydrogen storing metal alloy which has AB₅ mold structure shown with the presentation of $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{aluminum}_{0.3}$ was ground using the wet ball mill, and the hydrogen storing metal alloy powder whose mean particle diameter is 25 micrometers was manufactured. And the thickener (polytetrafluoroethylene) was added to this hydrogen storing metal alloy powder, and the paste was prepared. After applying this paste to the punching metal and drying, the punching metal was pressurized and cut in the electrode size for the cells of AA size, and the negative electrode was obtained.

[0055] (Manufacture of a separator) Paper making of the polyolefine system assembled-die fiber whose diameter of average fiber is 10 micrometers was carried out by the wet paper-making method, and the amount of eyes obtained the nonwoven fabric of 50-60g/m². After carrying out division processing by the high-pressure stream method and making this nonwoven fabric detailed, the pressure was stuck by pressure and regulated with the heat calendering roll, and thickness was set as 0.12-0.15mm, and permeability was set as the 10-20cc/[cm]²/second. Next, this nonwoven fabric was immersed into the vinyl monomer solution containing a photosensitizer, and ultraviolet rays were further irradiated to the nonwoven fabric concerned. This obtained the separator with which the carboxyl group was introduced. It was made into the amount of exchange of potassium ion, the amount of carboxyl groups, i.e., the ion-exchange ability, of this separator, and it was 0.2 - 0.5 milliequivalent /g.

[0056] (Manufacture of a nickel hydrogen battery) On both sides of the above-mentioned separator, an above-mentioned positive electrode and an above-mentioned negative electrode were involved in, and this has been arranged in a cylindrical case. And the electrolytic solution which consists of a potassium-hydroxide water solution was poured in into the case, and capacity manufactured the cylindrical alkaline battery (nickel hydrogen battery) of 1,500mAh(s).

[0057] Except for the point only using what performed corona discharge treatment, the same nickel hydrogen battery as the case of an example 18 (capacity = 1,500mAh) was manufactured to the nonwoven fabric before the carboxyl group installation obtained in the manufacture process of the separator in an example 18 as example 19 separator.

[0058] The positive electrode was manufactured like the case of an example 18 only using the example of comparison 2 1st component (namely, ** which does not mix the 2nd component to the 1st component). And except for the point using this positive electrode, the same nickel hydrogen battery as the case of an example 18 (capacity = 1,500mAh) was manufactured.

[0059] Constant-current discharge was carried out after it kept each nickel hydrogen battery of evaluation 4 examples 18 and 19 and the example 2 of a comparison at 20 degrees C and it carried out constant-current charge according to the charging current of 0.1CmA(s) in this condition for 15 hours until cell voltage was set to 1.0V by the discharge current of 0.2CmA. After the capacity of each cell was stabilized (after the charge-and-discharge capacity of each cell carries out abbreviation coincidence), constant-current charge of each cell was carried out by the charging current of 0.1CmA(s) for 15 hours, and it was saved for one week within the 45-degree C thermostat. During the retention period, day by day [1], it discharged until cell voltage was set to 1.0V by the discharge current of 0.2CmA(s), keeping each cell at 20 degrees C, and day by day, remaining capacity was measured. It was based on the result and asked for change of the capacity retention of each cell in a retention period. A result is shown in drawing 6. Even if the cell of an example 18 is after one-week preservation, compared with the cell of an example 19 and the example 2 of a comparison, its capacity retention is high about 15%, and it turns out that it is hard to carry out self-discharge so that clearly from drawing 6.

[0060] Moreover, in 70 degrees C, constant-current charge of the cell of examples 18 and 19 and each cell of the example 2 of a comparison was carried out by the charging current of 0.1CmA(s) for 15 hours, and elevated-temperature charging efficiency was investigated as compared with the charge capacity at the time of charging the charge capacity at that time on these conditions in ordinary

temperature (20 degrees C). A result is shown in drawing 7 . In addition, in drawing 7 , the charging efficiency of 70 degrees C makes charging efficiency of 20 degrees C criteria (100%), and shows it at a rate to it. Moreover, 45 degrees C shows the capacity retention after one-week preservation to drawing 7 collectively. Since the separator of the above-mentioned description is used for the cell of an example 18 in the positive electrode, including the 2nd component, drawing 7 shows excelling in capacity retention compared with an example 19, and excelling in both elevated-temperature charging efficiency and capacity retention compared with the example 2 of a comparison.

[0061]

[Effect of the Invention] It can realize the alkaline battery in which high charging efficiency is shown, maintaining a high-rate-discharge property, even if it is the case where cell temperature is an elevated temperature, since the nickel electrode active material for alkaline batteries of this invention contains the 1st component of a nickel hydroxide system, and the 2nd component containing one sort of elements chosen from the specific element group.

[0062] Moreover, it shows high charging efficiency, maintaining a high-rate-discharge property, even if it is the case where cell temperature is an elevated temperature, since the above-mentioned nickel electrode active material concerning this invention is used for the alkaline battery of this invention. When an above-mentioned thing is used as a separator, especially this alkaline battery is excellent in capacity retention, and cannot carry out self-discharge easily.

[0063] Furthermore, since the initial chemical conversion approach of the alkaline battery concerning this invention includes the process which charges the alkaline battery of this invention in a predetermined cell temperature requirement, it can raise more the charging efficiency at the time of the elevated temperature of the alkaline battery concerned.

[Translation done.]